



Molecular structure and sour gas surface chemistry of supported K₂O/WO₃/Al₂O₃ catalysts

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ABSTRACT

Molecular structures of the unpromoted and K₂O-promoted supported WO₃/Al₂O₃ catalysts were studied with *in situ* Raman and UV–vis spectroscopy. *In situ* Raman spectra revealed that supported 20% WO₃/Al₂O₃ corresponds to near monolayer coverage of isolated and oligomeric surface WO_x species on Al₂O₃. Above monolayer surface WO_x coverage (21% WO₃/Al₂O₃), crystalline WO₃ nanoparticles are also present. The addition of K₂O to the supported WO₃/Al₂O₃ catalyst increased the concentration of isolated surface WO_x species and did not form K₂WO₄ nanoparticles. The reducibility of the tungsten oxide structures depends on their structures (2D or 3D) and the K₂O promoter. Their interaction with acidic CO₂ and SO₂ gases was also investigated. Adsorption of CO₂ creates several surface carbonate species of varying acidity that were detected using a combination of *in situ* IR and mass spectroscopy. Adsorbed bicarbonate form on weakly basic surface sites on tungsten oxide monolayer WO₃/Al₂O₃ catalyst as well as in the presence of low 2.5% K₂O loading. At high 5% K₂O loading, the presence of the strong surface basic sites yields adsorbed carbonates. After SO₂ pretreatment, however, new strongly adsorbed sulfate appears on the surface that inhibits CO₂ adsorption.

1. Introduction

Abundant, yet difficult to utilize *sour* natural gas contains a large number of acidic components such as CO₂ and H₂S at quite high concentrations. Approximately 40% of the world's conventional natural gas reserves contain significant amounts of H₂S and CO₂ while about 30% contain < 15% CO₂ and 1–15 % H₂S [1]. These sour gas concentrations are treatable with conventional methods such as amine absorption/desorption [2–4], but the question remains whether this can be achieved economically. A major problem of conventional sour gas removal from natural gas remains utilization of the large amounts of environmentally non-friendly CO₂ and H₂S byproducts. Conventionally, the acidic CO₂ is emitted into the atmosphere acting as a major greenhouse gas motivating the need for new catalytic methods of converting CO₂ into hydrocarbons [5–7]. The H₂S, however, is a sour gas with high toxicity that is oxidized *via* the Claus process to yield unreactive elemental sulfur that can be used for the manufacture of sulfuric acid or deposited in chemical landfills [8]. An alternative is to directly convert H₂S and carbon oxides with the addition of H₂ to form

the reactive CH₃SH intermediate that can be further converted to a mixture of paraffin and olefins to avoid the high conventional CH₄-CO₂-H₂S separation costs [9–16]. Early studies have revealed the catalytic activity of supported tungsten based catalysts for such reaction, as well as the promotional effect of K₂O [17–20]. For example, Barrault et al. have achieved high selectivity towards two major products of CO (49%) and CH₃SH (51%) from a mixture of CO₂, H₂S and H₂ by using a supported 10% K₂WO₄/γ-Al₂O₃ catalyst [20].

As a widely used catalyst, supported WO₃/Al₂O₃ is active for a variety of reactions such as alkane metathesis [21,22], hydrogenation [23,24], dehydration [25,26], hydro-desulfurization [27,28] and hydrocarbon cracking [29,30]. Its molecular structure and surface chemistry have been extensively investigated in the literature, showing the existence of isolated, oligomeric and crystallized WO_x species depending on catalyst loadings [31–33]. Addition of K₂O has been found to play an important role as a promoter for the supported WO₃/Al₂O₃ catalyst and favors the production of methyl mercaptan from methanol and hydrogen sulfide [34]. Much less research, however, has been dedicated to elucidating the structure of the K₂O-promoted supported

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WO_x/Al₂O₃ catalyst.

In this work, we aim at elucidating the promotional effect of K₂O to WO₃/Al₂O₃ catalyst with an emphasis on its modification of surface chemistry, especially the interplay with two weakly adsorbed reactant molecules including H₂ and CO₂. In addition, the performance of competitive CO₂ adsorption under sulfur containing acidic environment was evaluated with the aid of SO₂ pre-adsorption. The application of modern characterization techniques including STEM, *in situ* Raman, *in situ* UV–vis, *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), H₂ temperature programmed reduction (TPR) and CO₂ temperature programmed desorption (TPD) has enabled the understanding of the surface chemistry for K₂O promoted WO_x/Al₂O₃ catalyst. Those fundamental insights will have the potential to guide the rational design of improved tungsten based catalysts for direct methyl mercaptan synthesis from sour natural gas.

2. Experimental

2.1. Catalyst preparation

Ternary K₂O promoted WO₃/Al₂O₃ catalysts (K₂O/WO₃/Al₂O₃) were synthesized with incipient-wetness impregnation method using water soluble ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀·xH₂O) and potassium hydroxide (KOH) as precursors [35,36]. The active catalyst support was Toyota γ-Al₂O₃ with surface area 170 m²/g. The synthesis involved two separate steps. In particular, tungsten oxide was initially impregnated into the γ-Al₂O₃ support and followed by impregnation of K₂O in the second step. Specific amount of ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀·xH₂O) was placed into a ceramic crucible, dissolved in 1 ml of deionized water and 1 gram of γ-Al₂O₃ was added into the ceramic crucible and stirred for 30 min. The samples were dried under ambient conditions overnight, further dried at 120 °C for 16 h and finally calcined at 500 °C for 4 h.

2.2. Scanning transmission electron microscopy

The morphology of the catalyst particles was investigated using a dedicated Scanning Transmission Electron Microscope (STEM) (Hitachi 2700 C) operating at 200 kV.

2.3. *In situ* UV–vis diffuse reflectance spectroscopy (DRS)

In situ UV–vis DR spectra of WO₃/Al₂O₃ and K₂O/WO₃/Al₂O₃ catalysts were obtained using a Cary 5000 UV–vis NIR spectrometer. The samples were loaded into an *in situ* cell (Harrick, HVC-DR2) and dehydrated under the flow of 10% O₂/He at 400 °C for 1 h. A magnesium oxide sample was used as the reflectance standard for collecting baseline in the 200–800 nm region.

2.4. *In situ* Raman spectroscopy

Raman spectra were collected using a LabRam-HR spectrometer (Horiba-Jobin Yvon) equipped with a confocal microscope, 2400/900 grooves/mm gratings and a notch filter. The 532-nm visible laser was focused on the samples using a confocal microscope equipped with a 50× long working distance objective (Olympus, BX-30- LWD). The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN₂-cooled CCD detector (Horiba, CCD-3000V). Catalyst samples were placed in an environmentally controlled high-temperature cell reactor (Harrick). Dehydrated spectra were collected after catalysts were dehydrated in the stream of 10% O₂/Ar at 400 °C for 1 h.

2.5. H₂-temperature programmed reduction (TPR) spectroscopy

The H₂-TPR experiments were carried out using an Altamira

Instruments (AMI-200) connected to a TCD detector. Approximately 30 mg of catalyst was loaded into a U-tube sample holder for analysis. The catalysts tested were first dehydrated under 10% O₂/Ar at 400 °C for 1 h then cooled down to 100 °C. The H₂-TPR experiments were then performed by ramping up the temperature under 10% H₂/Ar (30 ml/min) at a rate of 10 °C/min.

2.6. CO₂-temperature programmed desorption (TPD) spectroscopy

The CO₂-TPD experiments were performed using an Altamira Instruments system (AMI-200) with a TCD detector. Approximately 50 mg of catalyst was loaded into a U-tube sample holder for analysis. The catalysts tested were first dehydrated under 10% O₂/Ar at 400 °C for 1 h then cooled down to room temperature. The catalysts were then saturated under CO₂ flow for 1 h and flushed with He for 30 min. After the He flush, the CO₂-TPD experiments were performed by ramping the temperature under He at a rate of 10 °C/min.

2.7. Surface chemistry and acidity

Catalyst surface acidity was examined using a combination of NH₃ probe molecule and infrared spectroscopy. A Thermo Nicolet iS50 infrared spectrometer equipped with a Mercury-Cadmium-Tellurium (MCT) liquid nitrogen cooled detector was used with a Harrick Praying Mantis™ diffuse reflection accessory and ZnSe windows for determination of the acid sites. Catalysts were initially dehydrated by heating to 400 °C (heating rate of 10 °C/min) and holding at 400 °C for 1 h under air flow (30 mL/min). The *in situ* IR spectra were collected under N₂ (30 ml/min) while cooling down at 400 °C, 300 °C, 200 °C and 120 °C. Subsequently, N₂ was replaced with a flow of 1% NH₃/N₂ (30 mL/min; 30 min). Physisorbed NH₃ was removed by flowing N₂ (30 mL/min; 30 min). Spectra were then continuously recorded every minute during the temperature programming until 400 °C under 30 ml/min N₂ flow. The spectra of dehydrated catalysts at specified temperatures were subtracted from the spectra containing contributions of the catalyst and adsorbed NH₃ surface species at the same temperature.

2.8. *In situ* diffuse reflectance infrared fourier transformed spectroscopy (DRIFTS)

DRIFTS experiments were performed using diffuse reflectance mode in a Thermo Nicolet Nexus 670 spectrometer. Quadrupole mass spectrometer (Omnistar GSD-301 O₂, Pfeiffer Vacuum) was used to analyze the reaction products from the DRIFTS cell (Pike Technologies HC-900). Catalyst samples were first dehydrated under 5%O₂/He at 500 °C for 1 h and then cooled down to room temperature. After that, 30 ml/min CO₂ (2% CO₂/N₂) was introduced for 30 min, followed by a 20-min flush with He. The samples were then heated up to 500 °C under He with a rate of 10 °C/min. The catalysts then were cooled down to room temperature again, pre-treated with 30 ml/min SO₂ (210 ppm) for 30 min and flushed with He for 20 min. The pretreated samples were further saturated with CO₂ by flowing 30 ml/min 2% CO₂/N₂ for 30 min and flushed with He for 20 min and subsequently heated up under flowing He to 500 °C with a rate of 10 °C/min.

3. Results and discussion

3.1. Surface structure

The detailed composition, K/W atomic ratio and BET surface areas of all prepared catalysts were shown in Table 1. The Eg values were also calculated and provided from the corresponding *in situ* UV–vis spectra under dehydrated conditions (Fig. 1). Those values are within the range of oligomers of WO₆ (2.8 eV) and isolated WO₄ units (5.2 eV), indicating the coexistence of isolated and oligomeric species [37]. The smaller Eg value for 20% WO₃/Al₂O₃ than 21% WO₃/Al₂O₃ reflects the

Table 1

Composition, K/W atomic ratio, BET surface area and *in situ* UV-vis DRS Eg values for dehydrated supported $\text{WO}_3/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts.

Sample	K/W atomic ratio	BET (m^2/g)	Eg (eV)
Al_2O_3	–	133	–
21% $\text{WO}_3/\text{Al}_2\text{O}_3$	–	99	4.1
20% $\text{WO}_3/\text{Al}_2\text{O}_3$	–	105	4.5
2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$	0.65	113	4.5
5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$	1.26	95	4.9

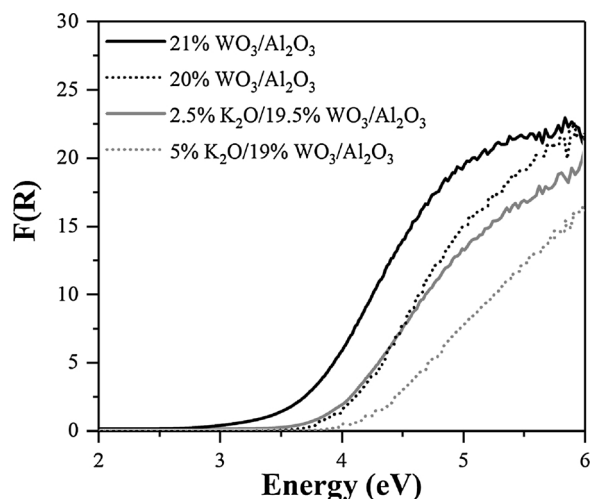


Fig. 1. *In situ* UV-vis spectra of dehydrated 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ and 5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts.

presence of a greater amount of oligomeric tungsten oxide component in the latter catalyst. Adding small amount of potassium oxide (K/W = 0.65) has negligible effect on UV-vis Eg value as well as the relative populations of isolated and oligomeric surface WO_x species. The addition of more potassium oxide (K/W = 1.26), however, increases the UV-vis Eg value to 4.9 eV, reflecting an increase in the population of isolated surface WO_x species at the expense of the oligomeric surface WO_x species.

Catalyst surface information and the interaction between K and W species were further studied with *in situ* Raman. Crystalline WO_3 exhibits strong and sharp Raman bands at 273, 719 and 809 cm^{-1} , while crystalline K_2WO_4 possesses strong and sharp Raman bands at 324 and 927 cm^{-1} , reflecting the presence of oligomeric WO_6 and isolated WO_4 sites in the WO_3 and K_2WO_4 crystals, respectively [37]. The Raman spectrum of supported 20% $\text{WO}_3/\text{Al}_2\text{O}_3$ exclusively exhibits a band at 1021 cm^{-1} and is assigned to surface WO_x species on the Al_2O_3 support, which is also confirmed by STEM image (Figs. 2b, S1). The Raman band at 1021 cm^{-1} corresponds to the stretching mode of isolated and oligomeric mono-oxo $\text{O}=\text{WO}_{4/5}$ surface species [32]. Supported 21% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst contains the surface $\text{O}=\text{WO}_{4/5}$ species (1021 cm^{-1}) and crystalline WO_3 nanoparticles (NPs) with strong characteristic bands at 260, 327, 711 and 804 cm^{-1} . The much stronger intensity for crystalline nanoparticles is due to the higher Raman cross sections. The Raman spectra for the K-promoted 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ and 5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts exhibit the $\text{W}=\text{O}$ bands at 985 cm^{-1} and 963 cm^{-1} with the absence of crystalline K_2WO_4 bands [38]. The shift of the $\text{W}=\text{O}$ Raman band from 1021 to $963\text{--}985 \text{ cm}^{-1}$ indicates that the potassium is interacting with the surface WO_x species and reflects lengthening of the $\text{W}=\text{O}$ bond [33].

3.2. H_2 -TPR

The interaction of the supported 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ and 5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts

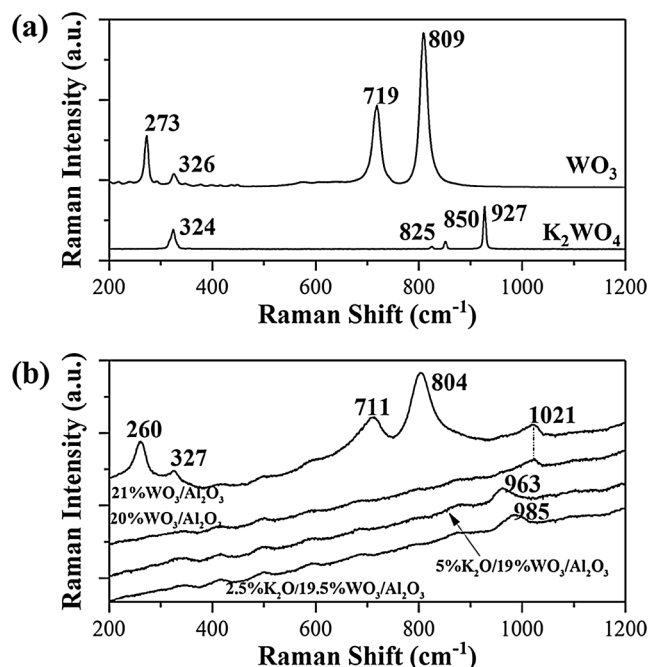


Fig. 2. (a) Raman spectra of crystalline WO_3 and K_2WO_4 . (b) *In situ* Raman spectra of dehydrated 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ and 5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts.

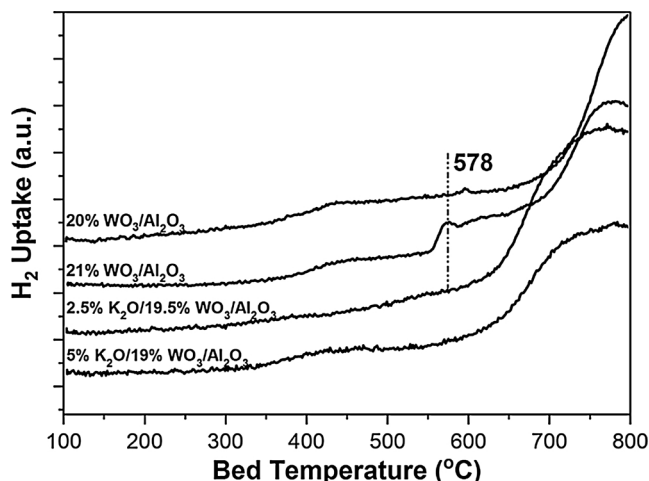


Fig. 3. H_2 -TPR spectra of supported 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ and 5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts.

with H_2 molecules was assessed with H_2 -TPR and the results are shown in Fig. 3. All four catalysts exhibited reduction peak at a temperature higher than 600°C , corresponding to the reduction of surface tungsten oxide species. Such a high reduction temperature has also been previously confirmed both theoretically and experimentally [39,40]. The supported 21% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst possesses an extra reduction peak at 578°C that is assigned to the reduction of crystalline WO_3 NPs [41,42]. Addition of K_2O to the catalyst shifted the reduction peak of surface tungsten species to lower temperature ($T_p \sim 725^\circ\text{C}$) and is probably due to enhanced H_2 adsorption or dissociation on K atoms.

3.3. CO_2 -TPD

The desorption of CO_2 , SO_2 and H_2O from dehydrated catalysts, with and without SO_2 pretreatment, during temperature programming are shown in Fig. 4 (a–d). In the absence of SO_2 pretreatment, the supported 20% $\text{WO}_3/\text{Al}_2\text{O}_3$ and 21% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts exhibit poor

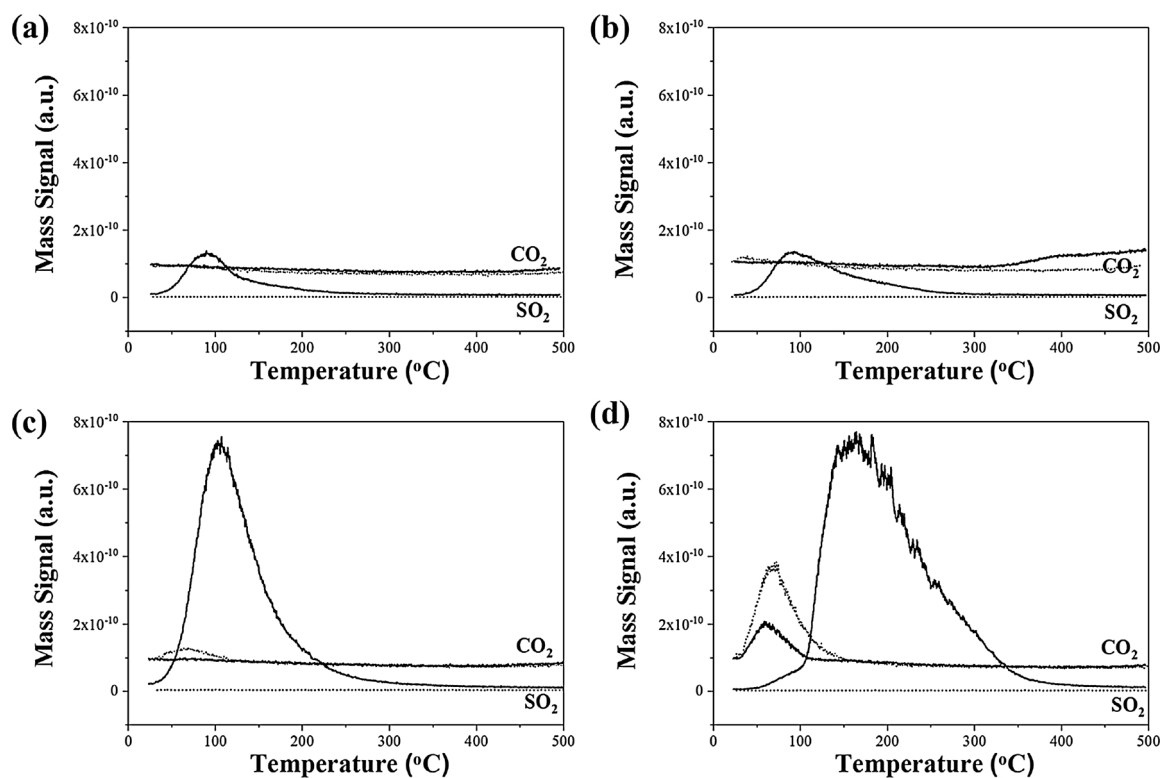


Fig. 4. (a–d) Mass spec signal of CO_2 and SO_2 obtained during CO_2 -TPD of catalysts with and without SO_2 pretreatment. (a) 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, (b) 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, (c) 2.5% $\text{K}_2\text{O}/19.5\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$, (d) 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$. The solid lines represent the sample with SO_2 pretreatment and the dot lines represent the sample without SO_2 pretreatment.

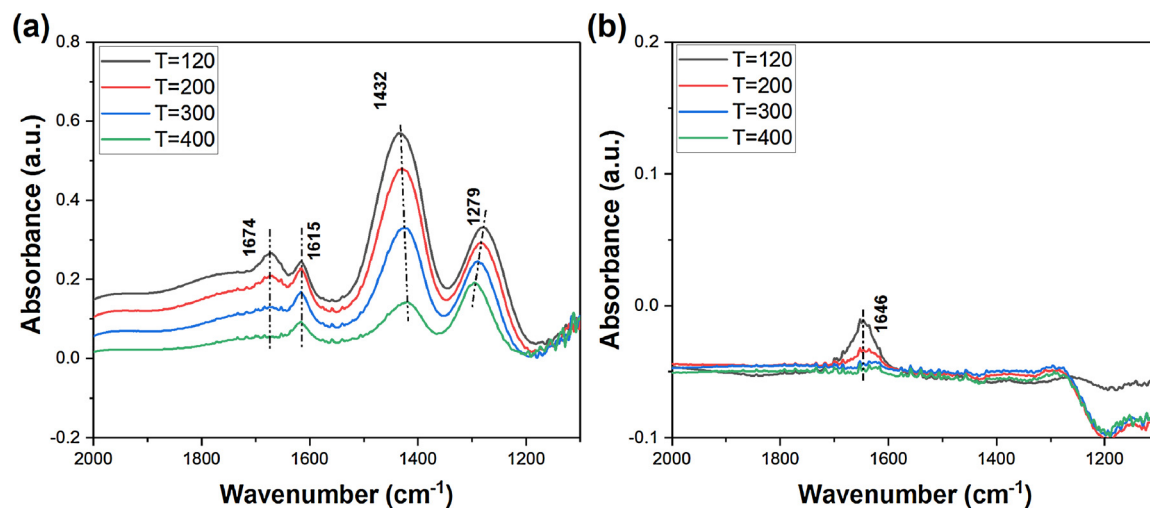


Fig. 5. NH_3 -IR spectra obtained from (a) 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, (b) 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$.

CO_2 adsorption capacity with barely a trace of CO_2 desorption at $\sim 50^\circ\text{C}$ (see Fig. 4 (a and d)) because acidic CO_2 very weakly interacts with the acidic surface WO_x sites [43]. The absence of CO_2 adsorption capacity of these two supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts reflects the presence of a surface WO_x monolayer that covers the basic sites of the alumina support. The addition of potassium oxide enhances CO_2 adsorption as reflected by CO_2 desorption at $\sim 50^\circ\text{C}$ because of the interaction of acidic CO_2 with basic surface K_2O sites. The CO_2 adsorption capacity of the dehydrated catalysts follows the order 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3 > 2.5\%$ $\text{K}_2\text{O}/19.5\%$ $\text{WO}_3/\text{Al}_2\text{O}_3 > 20\%$ $\text{WO}_3/\text{Al}_2\text{O}_3 > 21\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$.

The adsorption capacity of SO_2 on the catalysts is shown in Fig. 4 and is significantly greater than that of CO_2 because of the stronger acidity of SO_2 compared to CO_2 . Unlike the very weak CO_2 adsorption

on the K-free supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts, SO_2 modestly adsorbs on the K-free supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts. The adsorption capacity of SO_2 greatly increases, by $\sim 5\times$, with K_2O content because of the increased number of surface basic sites introduced by potassium oxide.

Although there is no H_2O desorption for the catalysts not pretreated with SO_2 , as expected for the dehydrated catalysts, all the supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts exhibit H_2O desorption after SO_2 pretreatment (Fig. S2). The amount of H_2O desorbed appears to decrease with potassium oxide promotion. The formation of H_2O after SO_2 treatment suggests that SO_2 is either reacting with alumina surface hydroxyls or making the catalyst hygroscopic and retains the trace moisture in the environmental cell.

The weak CO_2 adsorption capability was further decreased from the catalysts, especially the K-promoted catalysts, when SO_2 was pre-

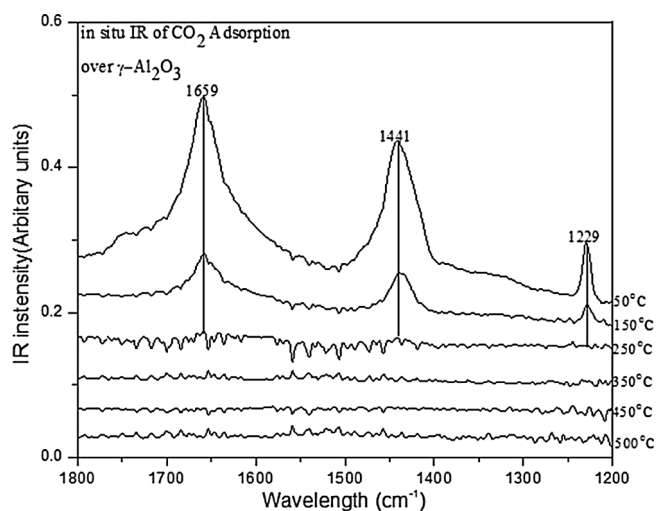


Fig. 6. IR spectra of γ - Al_2O_3 obtained at different temperature after CO_2 adsorption.

adsorbed on the catalysts. The supported 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalyst exhibited negligible CO_2 desorption indicating that acidic SO_2 coordinated to the basic surface K_2O sites and blocked coordinating of acidic CO_2 . The supported 5% $\text{K}_2\text{O}/19\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalyst however, still possesses CO_2 adsorption capacity after SO_2 pretreatment reflecting the presence of residual basic surface sites ($\sim 50\%$). The SO_2 pretreatment also appears to slightly weaken the CO_2 binding to the catalyst with T_p decreasing from ~ 75 to $\sim 60^\circ\text{C}$ when the supported 5% $\text{K}_2\text{O}/19\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalyst was exposed to SO_2 .

3.4. Surface acidity probed with NH_3 adsorption

The surface acidity of the dehydrated supported WO_x catalysts was probed with NH_3 -DRIFTS and the temperature dependent spectrum are presented in Fig. 5. After NH_3 adsorption at 120°C , the 20% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst (Fig. 5(a)) exhibits IR bands for both adsorbed NH_3 species (1615 and 1279 cm^{-1}) and NH_4^+ species (1674 and 1432 cm^{-1}) [44,45]. The existence of two type of adsorbed ammonia species clearly demonstrates that surface of the 20% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst possesses both Lewis (NH_3) and Brønsted (NH_4^+) acidity. Upon increasing the temperature, the population of the adsorbed NH_3 species decrease slower than surface NH_4^+ species that shows their greater stability on the surface. The NH_3 -IR spectrum for the supported 5% $\text{K}_2\text{O}/19\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalyst is shown in Fig. 5(b) and the addition of potassium greatly modifies the surface acidity of supported WO_x catalyst. The lack of the predominant 1279 cm^{-1} band for adsorbed NH_3 species and the 1432 cm^{-1} band for adsorbed NH_4^+ species suggest that K_2O completely suppressed both Brønsted and Lewis acidity from the surface WO_x species or exposed Al_2O_3 sites. The weak IR band at 1646 cm^{-1} , which diminishes at higher temperature, may arise from adsorbed ammonia species on K sites. Similarly, a sole band at 1610 cm^{-1} was observed for very low NH_3 coverages on $\text{Fe}\{111\}$ pre-covered with 0.25 monolayer of K and was attributed to antisymmetric deformation mode of ammonia, δ_a [46]. This vibration was attributed specifically to the interaction between ammonia and potassium atoms.

3.5. In-situ DRIFTS using CO_2 and SO_2 as acidic probe molecules

Carbonate in its free ion form has a Raman active vibration of 1063 cm^{-1} due to the symmetric C–O stretching (ν_1), an IR active

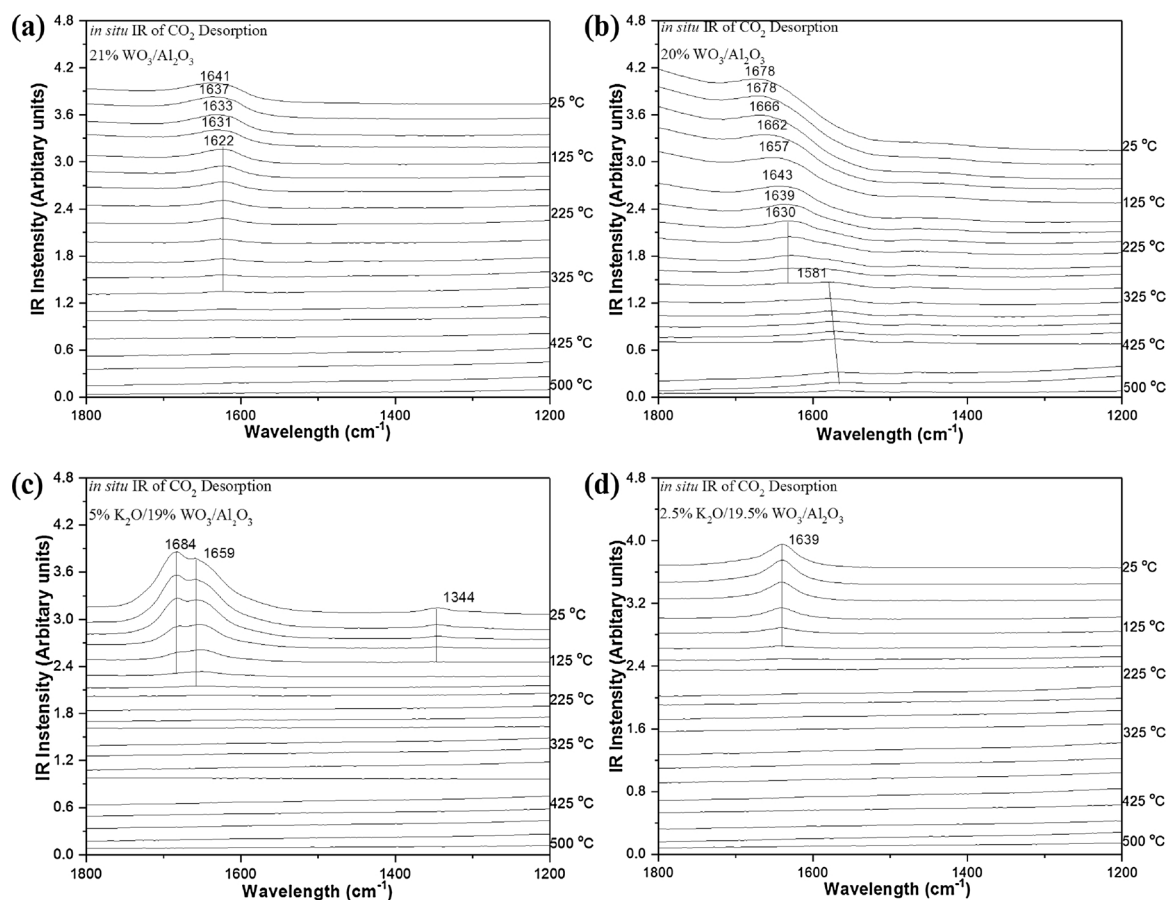


Fig. 7. (a–d) TP-IR spectra of CO_2 adsorption without SO_2 pretreatment obtained at different temperature. (a) 21% $\text{WO}_3/\text{Al}_2\text{O}_3$, (b) 20% $\text{WO}_3/\text{Al}_2\text{O}_3$, (c) 5% $\text{K}_2\text{O}/19\% \text{WO}_3/\text{Al}_2\text{O}_3$ catalysts and (d) 2.5% $\text{K}_2\text{O}/19.5\% \text{WO}_3/\text{Al}_2\text{O}_3$.

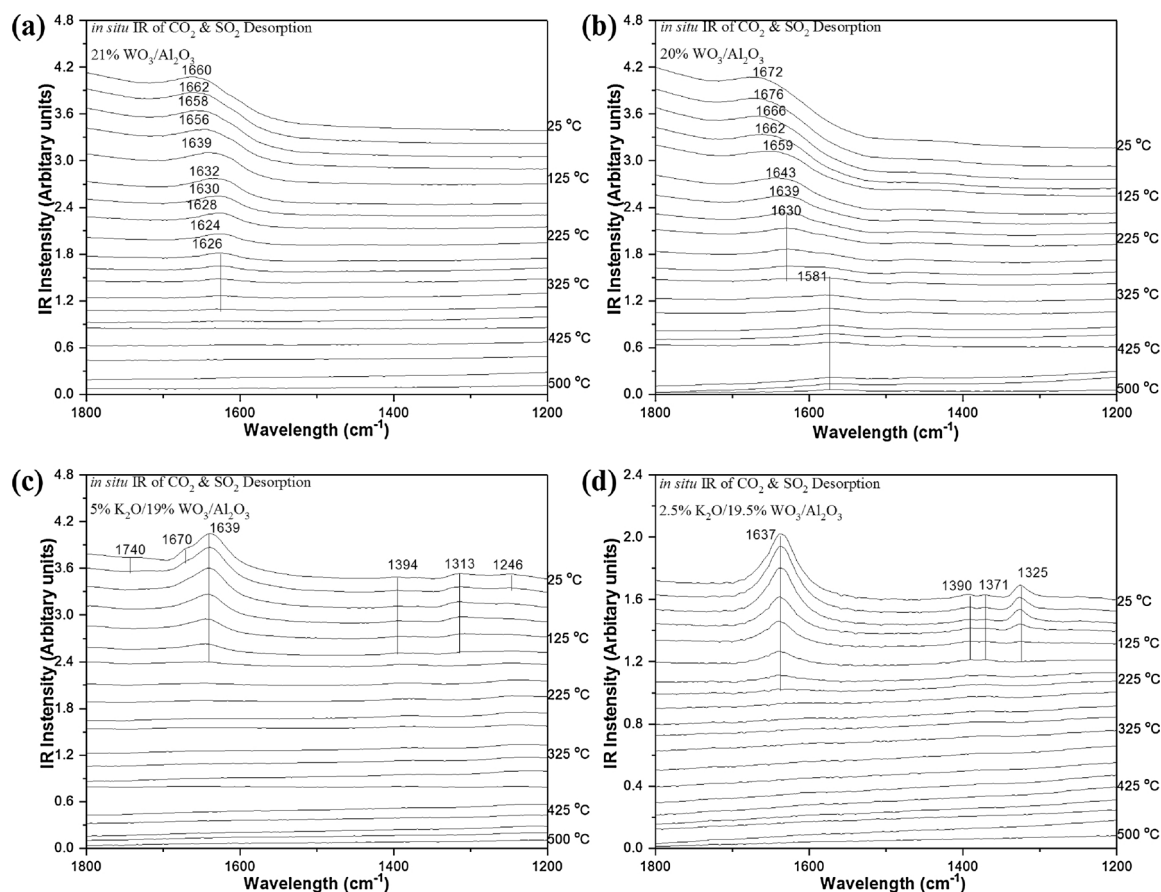


Fig. 8. (a–d) TP-IR spectra of CO₂ adsorption with SO₂ pretreatment obtained at different temperature. (a) 21% WO₃/Al₂O₃, (b) 20% WO₃/Al₂O₃, (c) 5% K₂O/19% WO₃/Al₂O₃ and (d) 2.5% K₂O/19.5% WO₃/Al₂O₃.

Table 2

Summary of surface CO₂ and SO₂ adsorption products on K₂O/WO₃/Al₂O₃ catalysts.

Condition	Samples	Wavelength (cm ⁻¹)						
Without SO ₂ pretreatment	21% WO ₃ /Al ₂ O ₃	1641						
	Assignment	Bidentate-II	Bicarbonate					
	20% WO ₃ /Al ₂ O ₃	1678						
	Assignment	Bidentate-II	Polydentate-I	Bicarbonate				
	5% K ₂ O/19% WO ₃ /Al ₂ O ₃	1684	1659	1344				
	Assignment	Bidentate-I	Bicarbonate	Monodentate				
	2.5% K ₂ O/19.5% WO ₃ /Al ₂ O ₃	1639						
Assignment	Bicarbonate							
With SO ₂ pretreatment	21% WO ₃ /Al ₂ O ₃	1660						
	Assignment	Bidentate-II	Bicarbonate					
	20% WO ₃ /Al ₂ O ₃	1672						
	Assignment	Bidentate	Polydentate-I	Bicarbonate				
	5% K ₂ O/19% WO ₃ /Al ₂ O ₃	1740	1670	1639	1394	1313	1246	
	Assignment	Bridged	Bridged	Bidentate-I	Al ₂ (SO ₄) ₃	Physisorbed SO ₂	Asymmetric O-C-O	
	2.5% K ₂ O/19.5% WO ₃ /Al ₂ O ₃	1637	1390	1371	1325			
Assignment	Bidentate-II	Al ₂ (SO ₄) ₃	Asymmetric O-S-O	Physisorbed SO ₂				

vibration of 879 cm⁻¹ due to out-of-plane deformation (ν_2), and two Raman-IR active vibrations of 1415 and 680 cm⁻¹, due to CO asymmetric stretching (ν_3) and in-plane deformation (ν_4), respectively [47,48]. Changes in molecular symmetry from electrostatic, hydrogen and covalent binding induce important shifts as well as the doubly degenerate ν_3 and ν_4 split. The magnitude of this ν_3 shift is attributed to different binding modes of the carbonate species formed. The surface species and their thermal stability on supported γ -Al₂O₃ after CO₂ adsorption has previously been well investigated in the literature [35,47]. Four types of surface chemisorbed carbonate species were identified: a) monodentate, 2) bidentate (1730–1660 and 1270–1230 cm⁻¹), 3)

bridged surface carbonate (~1900–1750 cm⁻¹ and 1180 cm⁻¹) and 4) bicarbonate (~3610–3605, 1650–1639, 1490–1440 and 1236–1225 cm⁻¹). The temperature-dependent *in situ* IR spectra of γ -Al₂O₃ obtained after CO₂ adsorption are presented in Fig. 6. Adsorption of CO₂ on γ -Al₂O₃ exhibits three peaks (1659, 1441 and 1229 cm⁻¹) that are attributed to surface bicarbonate species [47]. These are weakly bound to the alumina surface and completely desorb at 250 °C.

The temperature programmed-IR spectra of CO₂ adsorbed 20 and 21% WO₃/Al₂O₃ catalysts are shown in Fig. 7a and b, respectively. The 21% WO₃/Al₂O₃ catalyst (Fig. 7a) possesses a characteristic band at 1641 shifts to 1622 cm⁻¹, with increasing temperature and starts to

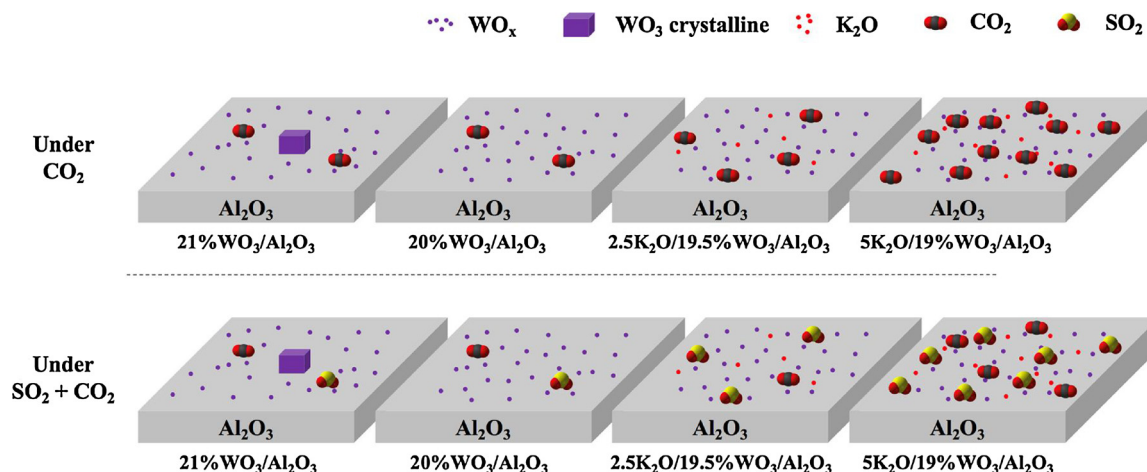


Fig. 9. Pictorial representation of the acid gas, CO_2 and SO_2 , interactions with $\text{WO}_3/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst surfaces.

desorb at 255 °C. The band position and desorbing temperatures (T_d) indicate the presence of bicarbonate species. Alternatively, this shift with temperature can be associated with transformation of adsorbed bicarbonate into more stable bidentate-II carbonate species. This is consistent with the release of gaseous H_2O observed in Fig. 4 where reactive surface hydroxyl recombine and desorb while adsorbed carbonate species are formed. The supported 20% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst (Fig. 7b) contains an IR band at 1678 that shifts to 1630 cm^{-1} at 225 °C. That band further transforms into a distinct high temperature-stable carbonate species at 325 °C. According to Figs. 2b and 3, both the supported 20 and 21% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts possess a distinct WO_x surface structure. It can be suggested that when WO_3 nanoparticles are absent on the surface WO_x monolayer the adsorbed CO_2 forms an adsorbed carbonate species at 1581 cm^{-1} . Strong CO_2 interactions with WO_3 nanoparticles, however, are not observed. A detailed literature review based on well-defined organometallic CO_2 -containing molecular infrared vibrations revealed that formate species can form with recorded vibration at 1612 cm^{-1} [47,49]. Other adsorbed CO_2 species on the W binding centers, such as $\mu_2\text{-}\eta^2$, with asymmetric C–O stretch at 1541 cm^{-1} or $\mu_2\text{-}\eta^3$ Class I at 1321 cm^{-1} are less likely since they are not stable at elevated temperatures [50,51].

The intensities of adsorbed CO_2 species increase for K_2O promoted catalysts, which is consistent with the CO_2 -TPD findings. For the supported 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst, three IR bands are observed at 1684, 1659 and 1344 cm^{-1} (Fig. 7c). The IR band at 1684 cm^{-1} represents bidentate-I species that desorbed at 150 °C. The IR band at 1659 cm^{-1} represented bicarbonate species that desorbed at ~125 °C. The IR band at 1344 cm^{-1} disappears much faster than the higher wavenumber peaks and can be associated with monodentate species that desorbed at ~50 °C. The 2.5% $\text{K}_2\text{O}/19.5\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst only exhibit a characteristic IR band at 1639 cm^{-1} (Fig. 7d) that starts to desorb at ~125 °C and is assigned to bicarbonate species.

The CO_2 temperature-programmed IR spectroscopy of the catalysts after the SO_2 pretreatment are presented in Fig. 8. Interestingly, the supported 20 and 21% $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts contain adsorbed species analogous to those shown in Fig. 7 after CO_2 adsorption with no obvious SO_2 species observed. This is due to the weak interactions between the SO_2 and $\text{WO}_3/\text{Al}_2\text{O}_3$ and different molar extinction coefficient for $\text{CO}_{2,\text{ads}}$ and $\text{SO}_{2,\text{ads}}$. On the $\gamma\text{-Al}_2\text{O}_3$ support, many surface species form depending on the termination of $\gamma\text{-Al}_2\text{O}_3$ and its degree of dehydration. In general, they range from weakly bound SO_2 coordinated to surface Al–OH, AlO or Al sites with vibrations at 1334, 1322, 1255–1189 cm^{-1} , respectively, while adsorbed sulfite, AlOSO_2 , exhibits a band at 1135 cm^{-1} [52,53]. The absence of these bands in Fig. 8a and b suggests limited availability of adsorption sites due to the near monolayer surface WO_x coverage.

For the supported 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst, the IR bands at 1740 and 1670 cm^{-1} represent the bridged carbonate species, and the bands at 1639 cm^{-1} are assigned to bidentate-I species which desorb at 150 °C. The band at 1394 cm^{-1} is assigned to the formation of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$ and the band at 1313 cm^{-1} is assigned to the physisorbed SO_2 species [40,52,53]. The supported 2.5% $\text{K}_2\text{O}/19.5\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst exhibits an IR band at 1637 cm^{-1} ($T_d = 255$ °C) that is attributed to bidentate-II species. The IR band at 1390 cm^{-1} is attributed to the formation of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$ [54]. The characteristic band at 1371 cm^{-1} represented the asymmetric stretching of the SO_2 vibration and the band at 1325 cm^{-1} is attributed to physisorbed SO_2 species [47,54,55]. The peak assignment of DRIFT spectra obtained under two different conditions are summarized in Table 2.

4. Conclusions

This work elucidates the fundamental aspects of the molecular structures and surface chemistry of supported $\text{WO}_3/\text{Al}_2\text{O}_3$ based catalysts in acidic gas CO_2 and SO_2 environments. Based on the data presented in Figs. 7 and 8, the pictorial representation of the complex interplay between the catalyst active sites and the adsorbed species is summarized in Fig. 9.

Surface WO_x species dominate un-promoted and K_2O -promoted supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts. For dehydrated supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts with high tungsten oxide coverage, the surface contain both isolated and WO_x sites. With increasing potassium oxide loading, the surface WO_x sites become more isolated. The isolated surface WO_x sites on Al_2O_3 are difficult to reduce while K_2O promotion improves reduction of surface WO_x sites at elevated temperatures. For the monolayer covered supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalysts, CO_2 adsorption results in weakly bound surface bicarbonate species and addition of K_2O changed both the surface carbonate speciation and the CO_2 adsorption capacity. The adsorption of CO_2 on the supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst mostly results in surface bidentate species. On the K_2O -promoted supported $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst, surface bidentate and monodentate species are mainly formed. After SO_2 pretreatment, the new sulfate stretching modes are observed over K_2O -promoted catalyst, but carbonate stretching vibrations also exist showing a competitive adsorption. With SO_2 pretreatment, the capacity of CO_2 adsorption was suppressed while supported 5% $\text{K}_2\text{O}/19\%$ $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst showed the best resistance. As a result, the promotion of K_2O for direct synthesis of methyl mercaptan from sour gas can be attributed to 1) enhanced H_2 adsorption and/or dissociation, 2) increased CO_2 adsorption and 3) improved resistance to strong acidic condition for CO_2 adsorption.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.03.044>.

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